DEVELOPMENT AND PILOT-SCALE IMPLEMENTATION OF AN NA- AND ENA-BASED REMEDIATION STRATEGY AT A REFINERY SITE WITH LARGE-SCALE PETROLEUM HYDROCARBON AND BTEX-CONTAMINATION

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INTRODUCTION

Industrial megasites like oil refineries are characterized by complex groundwater contamination patterns due to the complex input history (local spills, long-term leakages...) and the heterogeneity of the affected aquifer. The "traditional" investigation approach, a static plan of drilling, sampling, analyzing pre-defined grid points, reporting and then, afterwards, recognizing that the sampling points were poorly located, is absolutely inadaequate for this type of site. Our consortium recently developed an **A**daptive **S**ite **I**nvestigation **A**pproach (ASIA) and are currently applying (and optimizing) this approach at several megasites. It is worth to mention, that a pre-requisite for this approach is (1) the access to modern equipment like direct-push-technology, on-site GC-analytics and data handling and modelling tools and, also essential (2) a highly-qualified, interdisciplinary and inter-acting team.

This paper describes the application of this approach from one of Germany´s major crude oil refinery sites. The task in this case was to determine extension and intrinsic biochemical processes of two plumes, one of BTEX compounds, the other one of nitrate; a former fertilizer plant being the origin of the latter one. If the potential for Natural Attenuation (NA) can be quantified and conditions for it´s enhancement (ENA) can be estimated, NA/ENA at this particular part of the refinery could be of major importance for the cost-efficient remediation strategy for the whole megasite.

In a first step, the distribution of floating (or residual) LNAPL-phase was mapped by the measurement of radon-222 in the soil gas; a method developed by UFZ and adapted to direct-push-equipment to reach the necessary depth of around 5 m. Areas with LNAPL-phase then could be excluded from the further investigation steps.

Secondly, the subsurface structures were mapped by high-resolution electrical conductivity (EC) logging and the pre-existing geological-hydrogeological model could be improved to the necessary precision by almost real-time data transmission and input into the model.

After the localization of the hydraulically most important subsurface structures, in the next step *in situ*-groundwater sampling using 1-inch probing equipment and on site-chemical analyses were

performed. Again, the real-time input into the model allowed an instantaneous adaption of the sampling point localization.

In reality, the field work in this campaign was done during a period of around 8 working days, investigating an area of about two hectares down to a depth of around 15 m. The obtained results are of a remarkable degree of spatial resolution, which is absolutely necessary for the subsequent steps of small-scale flow and transport modeling currently in progress.

RADON MEASUREMENTS

One goal of the research program, which after all aimed to assess the NA potential at the site, was distinguishing between areas characterized by a BTEX phase floating on the groundwater table (LNAPL pool) and areas without such floating phase but with dissolved BTEX contaminating the groundwater (NAPL plume). Mapping of the radon distribution pattern in the soil gas close to the groundwater table was employed to tackle that task.

The radon method (SCHUBERT *et al.*, 2005, 2007a, 2007b; HÖHENER & SURBECK, 2004) is based on the generally strong affinity of radon to NAPL. Radon partition coefficients between complex LNAPL mixtures such as gasoline, diesel fuel, or kerosene and air (at room temperature) are in a range of about 10 and 12. Hence, if a residual organic phase is present in the subsurface, part of the radon, which occurs naturally in the soil gas, accumulates in the organic phase giving rise to reduced soil gas radon concentration in the close vicinity of the contamination due to that partitioning process. Consequently, a floating LNAPL pool results in significantly reduced radon concentrations in the soil gas close to the groundwater table. Since the soil gas radon concentration is on the one hand strongly influenced by floating NAPL but on the other hand not influenced by organic contaminants that appear dissolved in the groundwater, areas with floating LNAPL pools can clearly be told apart from areas outside of that zone but still inside the dissolved NAPL plume. Such differentiation would not be possible by BTEX analysis of groundwater samples alone.

Zones characterized by a soil gas radon deficit can easily be localized by means of conventional soil gas sampling and on-site analysis using a suitable gas pump and a standard radon monitor. Due to the direct availability of results on site the radon method allows for a straightforward localization of the NAPL pools that cause the local radon deficit. Radon soil gas measurements were performed at 27 points. Radon activity concentrations in the soil gas were detected using an ALPHAGUARD® system (Genitron) in combination with GEOPROBE® direct-push-technique to reach the necessary sampling depth of up to 5 m below surface. The results of the radon mapping are shown in Fig. 1. Relative activity concentrations of <50 % of the geogenic background value, which was found to be around 30 Bq/m^3 indicate the pres-

ence of LNAPL in the subsurface. The method does not allow the distinction between residual phase in the unsaturated zone and free, floating phase; however, the results were confirmed by the subsequent soil and groundwater sampling and the method has proven its suitability for mapping LNAPL phase distribution in the subsurface. These areas could be excluded from the further investigation steps.

DIRECT-PUSH INVESTIGATIONS

Objective of the high-resolution geological and hydogeochemical investigation was the identification and localization of degradation processes under nitrate- (or sulfate-) reducing conditions along the flowpath of the BTEX-plume. Due to the small-scale spatial hetero-
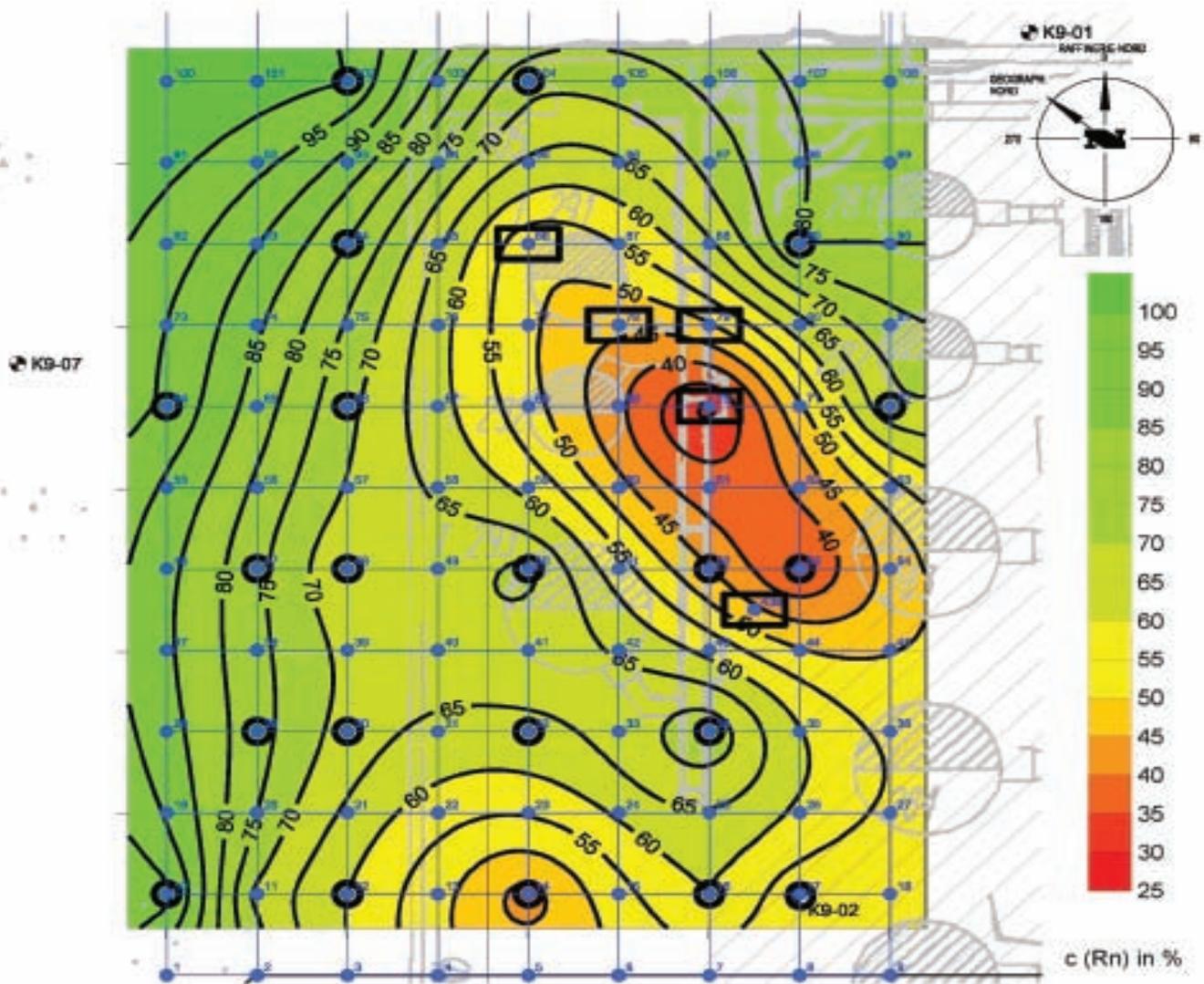

Fig 1   -   Distribution of relative ^{222}Rn acitity concentrations in the soil gas. Concentrations <50 % indicate the presence of LNPL-phase in the subsurface. Bold circles indicate radon measurement points; bold quadrangles represent LNAPL phase detected in groundwater samples

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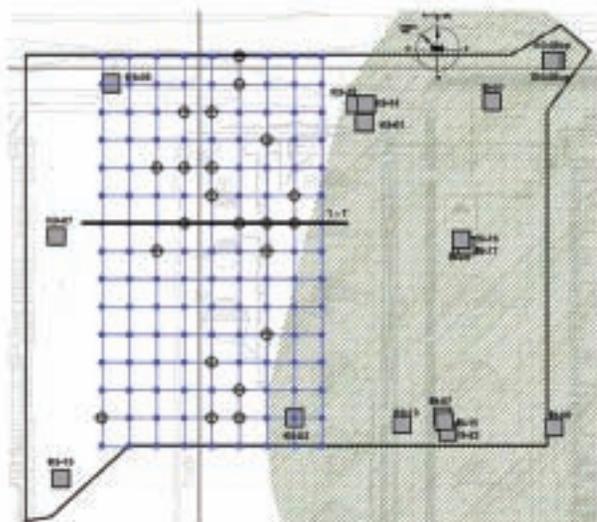
Fig. 2 - Position of grid spaced direct-push locations (circles) and sections. Grid spacing is 25 x 25 m. Quadrangles indicate previous groundwater observation wells. Bold lines across grid (1-1´ and 2-2´) indicate cross sections perpendicular and along groundwater flow direction. Hatched area indicates distribution of floating LNAPL

geneity of the Quaternary strata forming the geological framework, a narrow-spaced investigation grid of 25 x 25 m was chosen in the suspected area of the "interfingering" of both the nitrate and the BTEX plumes. Fig. 2 shows the position of the grid and the sections across the investigated area. At each grid point, a two-step direct-push probing

was executed, the first step being a electrical conductivity (EC) logging followed by an *in situ*-groundwater sampling. The direct-push-investigation at the test area were performed using a GEOPROBE 7740 machine with EC logging and groundwater sampling equipment. For methodological and technical details see DIETRICH & LEVEN, 2006.

ELECTRICAL CONDUCTIVITY (EC) LOGGING

The EC-logging was performed with vertical resolution of 5 cm; the correlation of electrical conductivity values and lithology was done after a calibration with a complete 15 m liner sample from the area. Fig. 3 illustrates the results of the high-resolution EC-logging, that yielded a significant improvement of the lithostratigraphic model of the area under investigation. The correlation between the 25 m spaced grid and the 5 cm resolution of the EC-data allowed the setting of the numerical flow model with a spacing of 5 m. This near-reality idea of the aquifer architecture is the base not only for the conceptual model of flow and reactive transport but is also essential for the interpretaion of hydrochemical data obtained in the same sampling campaign.

HYDROCHEMICAL INVESTIGATIONS

Objective of the hydrochemical investigations was the delineation and quantification of contaminant degradation processes at the test site. The special situation (presence of a distinct nitrate plume in a sulfate-rich groundwater environment) required the consideration of both substances as potential electron acceptors for the degradation of the BTEX compounds. Groundwater samples were taken using a 1-inch-direct-push filter unit (DIETRICH & LEVEN, 2005)) with a ver-
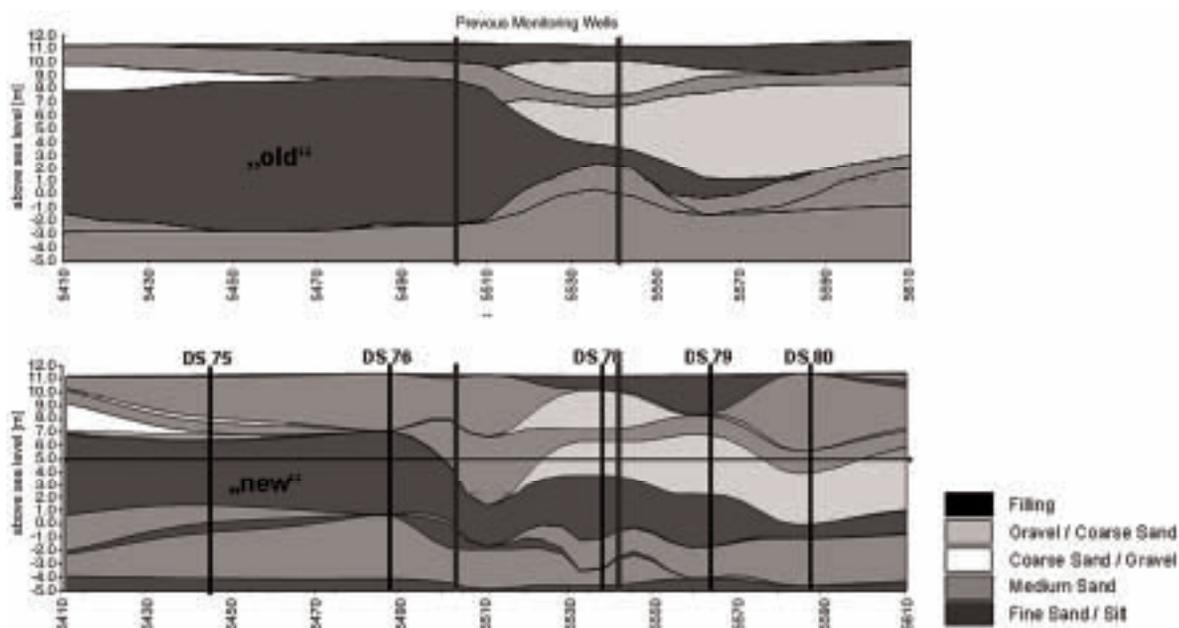

Fig. 3 - Comparison of "old" lithostratigraphic-geological model based on previous monitoring wells (above) and "new" model based on the direct-push investigations (points DS 76-80; below) along one W-E directed cross section (1-1´). Black horizontal line in lower section indicates groundwater level. Note vertical exaggeration!
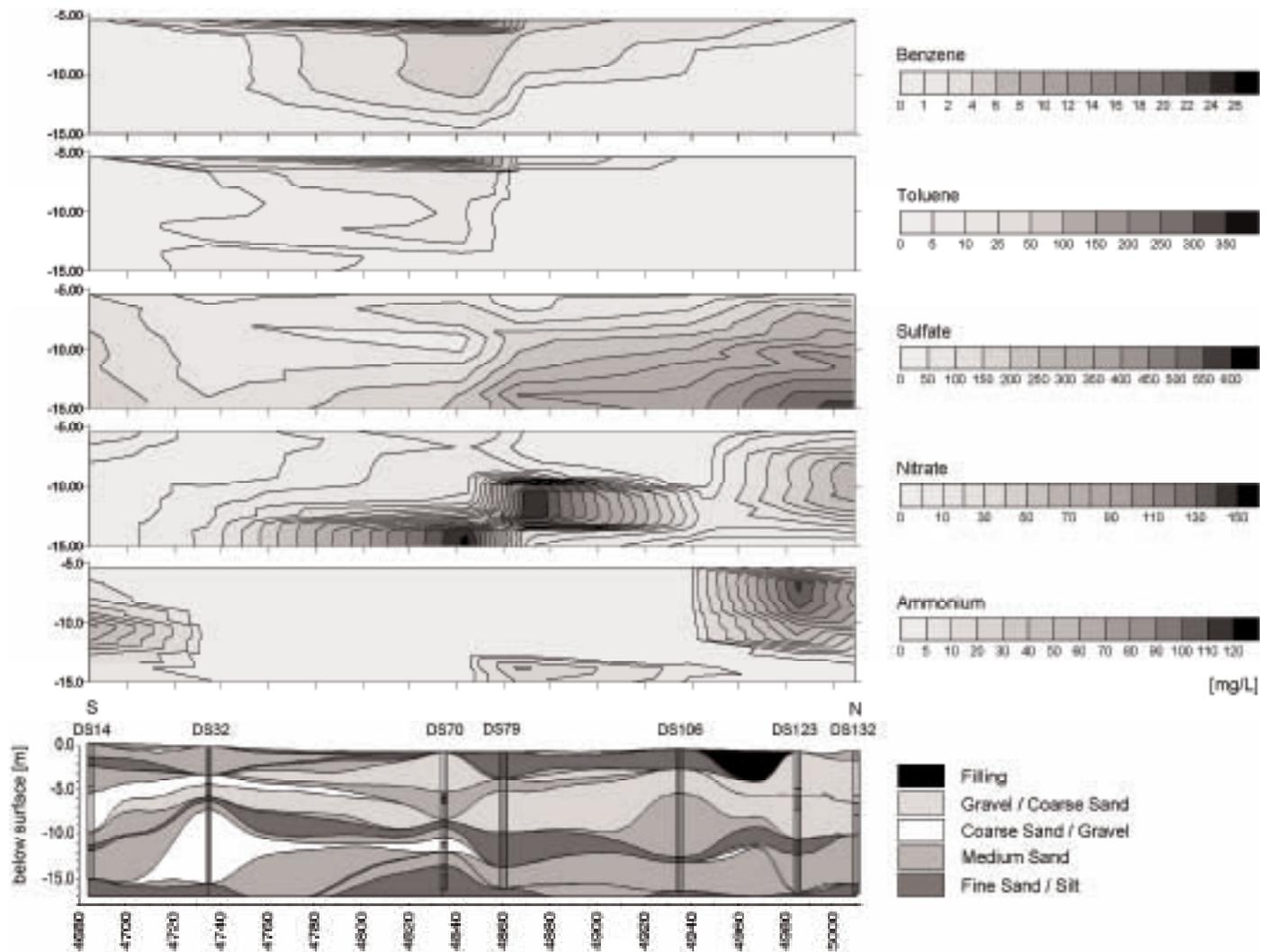
Fig. 4 - Distribution of contaminants (benzene and toluene) and electron acceptors (above) and geological model (below) along one S-N cross section (2 - 2´ in Fig. 3). Groundwater flow is from S to N. Note vertical exaggeration!

tical resolution of 1 m. The samples were analyzed according to ISO 10301 on site using a GC-MS system (MS:EM Bruker) for the detection of BTEX compounds and cuvette test kits (Dr. Lange AG) for nitrate, ammonia and sulfate. Fig. 4 shows an example for the obtained hydrochemical data along a cross section in groundwater flow direction. The picture shows clearly the strong correlation of electron acceptor depletion and contaminant concentration, indicating natural attenuation processes in the aquifer parts with the corresponding high hydraulic conductivities.

ADAPTIVE SITE INVESTIGATION APPROACH

The field data obtained by direct-push technique (depth, penetration velocity, EC-log) and on site analytics (ph, Eh, radon activ-

ity concentration, BTEX and electron acceptor concentrations) were generated, processed and pre-interpreted on site during the investigation campaign and transmitted directly to the central data base where the geological model was updated daily. The position for the next sampling points therefore could be optimised and realised on the following day. This adaptive planning approach has proven to be by far more cost-efficient than traditional approaches. Both the information quality by means of spatial resolution and parameter spectrum and the necessary time before a knowledge based decision on the suitability (less than two weeks) for the further development as a Natural Attenuation test site could have been achieved by the conventional approach of drilling, sampling, laboratory analytics and reporting.
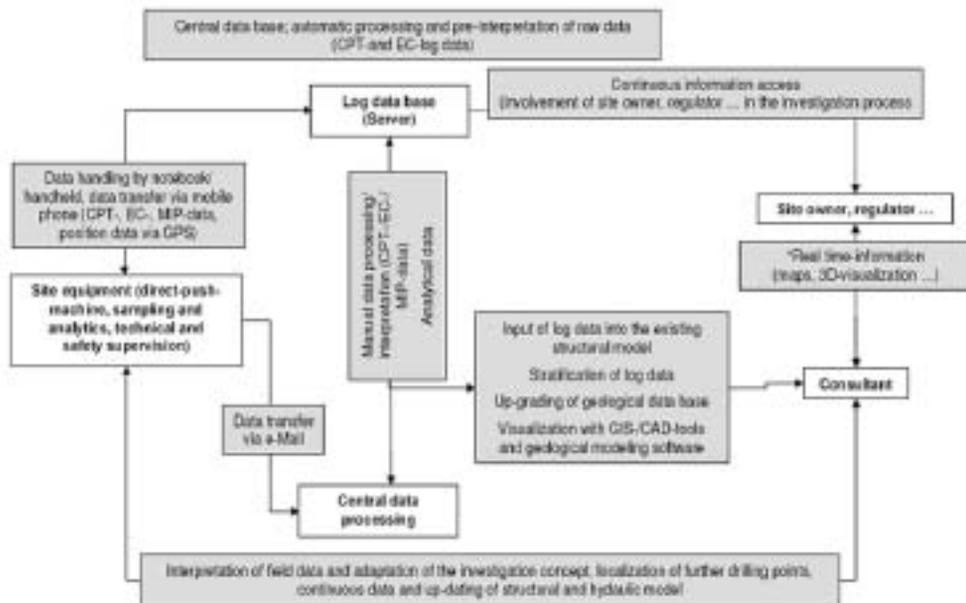
Fig. 5 -   Adaptive site characterisation approach using direct-push technique and on site analytics
Currently, the approach is extended to other site management-related issues like plume delineation, geochemical mapping, reactive transport modelling and risk assessment

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